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THE DECOMPOSITION OF AMMONIA BY IRON CATALYST MIXED WITH Al_2O_3 AND K_2O.

By Ryô Kiyama.

Many studies[1] have been done concerning the catalytic decomposition of ammonia and its catalysts, but there are few systematic studies on the influence of the components of a mixed catalyst. Using a catalyst consisting of Fe_3O_4, Al_2O_3 and K_2O, the present author examined the influence of the concentration of each component of the catalyst on the reaction in question.

Experimental

Materials

Ammonia used in the present experiment was a synthetic ammonia held in a bomb, which, was dried with soda lime and potassium hydroxide before use. Substances of high boiling points contained, such as grease used as the lubricating agent, were removed by distillation or by passing through a drying tube, while those of low boiling points were also removed by letting out from the bomb to the outside of the apparatus.

Hydrogen was obtained by electrolysis of water and nitrogen by the distillation of liquid nitrogen and both were dried by being passed through the drying tube.

Apparatus

In the measurements of the decomposition velocity and adsorption, variation in the pressure was observed by means of a spring manometer[2] made of Terex-glass. The reduction velocity of the catalyst was measured from the increase in the weight of the absorbent for the water formed by passing hydrogen at a given rate through the reaction vessel in which the catalyst was placed.[2]

Methods and the theory

Dr. S. Horiba,[3] Professor of the Kyoto Imperial University, and Dr. T. Ri have first found that such a catalytic decomposition proceeds stepwise in the following order—a reaction of retarded form at first and of the first order and then of the zero or the fractional order. This was fully examined theoretically and experimentally in the decomposition of CO by reduced nickel.

In the present case of the decomposition of ammonia, the same theory may be applied.

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1) Rideal and Taylor, *Catalysis in Theory and Practice*; Maxted, *Catalysis and its Industrial Application*; Schwab, *Katalyse*; Finkelstein, *Acta Physicochim.* I, 524, (1934).

2) The spring manometer used was of a semicircular shape (See this journal I, 269 (1927)), and the reaction vessel held about 100 c.c.

3) S. Horiba and T. Ri, This Journal (Japanese edition) 4, 123 (1930).

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Suppose that the surface of the catalyst consists of three differently active parts—*A*, *B*, and *C*. Again suppose that all these active parts adsorb NH_3 strongly: the most highly active part *A* adsorbs H_2, the decomposition product, more strongly than NH_3; the part *B* adsorbs H_2 as well as NH_3; the part *C* scarcely adsorbs H_2.

Then the reactions corresponding to the active parts *A*, *B*, and *C* are the reaction of retarded form, that of the first order and that of the zero or fractional order respectively, and these will appear consecutively in the course of the whole reaction in the above-described order, since the active parts become successively covered by the decomposition product.

Let the fraction of the active surface occupied by NH_3 be θ_{NH_3}, then we have, according to Langmuir's formula,

$$\theta_{NH_3}=\frac{b_{NH_3}p_{NH_3}}{1+b_{NH_3}p_{NH_3}+b_{N_2}p_{N_2}+b_{H_2}p_{H_2}},$$

where p and b are the pressure of each gas and its adsorption coefficient respectively. Let a and x represent the initial pressure of NH_3 and the pressure of NH_3 decomposed respectively, then the expression for the highly active part, such as *A*, becomes

$$\frac{b_{NH_3}(a-x)}{b_{NH_3}(a-x)+b_{H_2}x}.$$

It is considered that the velocity of decomposition at the initial stage is chiefly the velocity at the most highly active part *A*, and so the velocity equation is

$$\frac{dx}{dt}=k\frac{a-x}{b_{NH_3}(a-x)+b_{H_2}x}.$$

Integrating this, we have

$$(b_{NH_3}-b_{H_2})\frac{x}{t}+ab_{H_2}k_m=k. \quad \left(k_m=\frac{1}{t}\ln\frac{a}{a-x}\right)$$

Plotting k_m against x/t, we have a straight line of positive inclination as shown in Fig. 1, *A*. Now, when $x/t=0$

$$k_m=k/ab_{H_2}. \qquad (1)$$

This means that the larger $[k_m]_{x/t=0}$ is the smaller the value of b_{H_2} becomes. When $k_m=0$,

$$\frac{x}{t}=\frac{k}{b_{NH_3}-b_{H_2}}. \qquad (2)$$

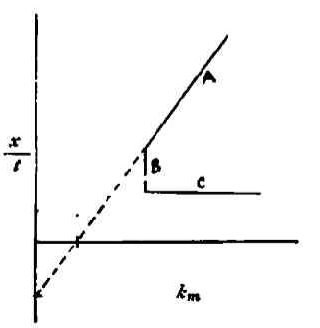

Fig. 1.

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As a relation $b_{NH_3} < b_{H_2}$ holds at the active part A, the larger $| b_{NH_3} - b_{H_2} |$ becomes the smaller $[|x/t|]_{k_m=0}$ becomes.

From the experimental data the values of k_m and x/t were calculated and then the values $[k_m]_{x/t=0}$ and $[x/t]_{k_m=0}$ were examined with respect to the composition of the catalyst.

The relation between the activity of the catalyst and its composition was also examined, taking the decomposition velocity as a measure of the catalytic activity.

Experimental Results

Reduction of the catalyst

5 g. of the sample was reduced to a powder of 100 mesh[4] at 440°C. in the atmosphere of hydrogen under the ordinary pressure. Any catalyst of the $Fe_3O_4-Al_2O_3-K_2O$ system is hard to reduce, and the percentage of the components leads to the variation in the reaction velocity.

As seen from Table I, when the amount of K_2O is unaltered, the increase in the amount of Al_2O_3 retards the reaction velocity. When the amount of Al_2O_3 is unaltered, the increased amount of K_2O (to 2%) tends to accelerate the velocity (Table II).

Table I.

Catalyst No.	Percentage of components		* Reduction velocity
	Al_2O_3	K_2O	
1	0**	1	74.7
2	2	1	62.7
3	5	1	63.9
4	10	1	50.2

* The values given here are relative.
** A small particle of aluminium was contained in iron, the material.

Table II.

Catalyst No.	Percentage of components		Reduction velocity
	K_2O	Al_2O_3	
5	0.5	5	50.2
3	1.0	5	63.9
6	1.5	5	69.1
7	2.0	5	73.3
8	5.0	5	60.0

Table III.

Catalyst No.	Percentage of components		Reduction velocity
	K_2O	Al_2O_3	
9	0.5	10	48.9
10	2.0	10	59.2

Table III again justifies the above-described fact that the increased amount of K_2O accelerates the reduction velocity, when the amount of Al_2O_3 is unaltered. But it is considered that the maximum limited amount of K_2O has some relationship to the amount of Al_2O_3.

4) The amount of the catalyst, whose particle was 100 mesh in size, was 5 g., unless specially mentioned.

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Adsorption by the catalyst

Adsorption of NH_3: At room temperature the pressure decrease of about 0.2 cm was observed under the initial pressure of 20 cm. Hg.

Adsorption of N_2: Though adsorption was observed at 440°C., the amount of adsorption was markedly small.

Adsorption of H_2: The amount of adsorption of H_2 was so large that it was measured at 300°, 440° and 500°C. under the initial pressure of 20 cm. Hg. One of the examples is given in Table IV.

Table IV.

Catalyst No.	Amount adsorbed cm³/g*		
	300°	440°	500°
1	1.08	1.42	2.28
2	0.40	0.44	0.83
3	0.37	0.65	1.01
4	0.13	0.33	0.46

* The amount is expressed by the decrease in the pressure of hydrogen.

It is noticeable in this table that the adsorbed amount by catalyst No. 2 is small in comparison, but it is admitted that the amount of adsorption of hydrogen generally decreases with the increase in the amount of Al_2O_3 when the amount of K_2O is constant. This fact has been justified by the measurements in the presence of different kinds of catalysts. The effect of the hydrogen adsorption of K_2O is uncertain yet.

Activity of the catalyst

Representing by $t\left(\frac{1}{4}\right)$ and $t\left(\frac{1}{2}\right)$ the times (minutes) which it takes to decompose $\frac{1}{4}$ and $\frac{1}{2}$ at 440°C. under the initial pressure of 10 cm. Hg respectively and by $t\left(\frac{1}{1}\right)$ the time elapsing in the completion of the decomposition, a comparison of these three was made as the standard of the activity. The result obtained is given in Table V.

In Nos. 1—4, the amount of K_2O is constant and that of Al_2O_3 gradually increased. The activity becomes high with the increased amount of Al_2O_3. In Nos. 5—8, the amount of Al_2O_3 is constant and that of K_2O increased by 0.5—5%. In Nos. 9 and 10, Al_2O_3 constitutes 10% as a component and the increase of its amount requires that of K_2O.

Table V.

Catalyst No.	Activity		
	$t\left(\frac{1}{4}\right)$	$t\left(\frac{1}{2}\right)$	$t\left(\frac{1}{1}\right)$
1	28	64	300
2	18	48	330
3	14	35	160
4	7	25	160
5	8	23	150
6	2	5	120
7	2	3	90
8	1	7	60
9	8	30	220
10	2	4	90

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The decomposition velocity, or the $\frac{x}{t}-km$ curve, under various conditions

1. The effect produced by the amount of the catalyst.

In all the experiments, to make the decomposition end within 5—6 hours, 5 g. of the catalyst, whose particle was made 100 mesh in size, was used.

As to the above-described three active parts——*A*, *B*, and *C*, the change of the $\frac{x}{t}-km$ curve caused by a decrease in the amount of the catalyst to 0.1 g. was examined. In the case when a small amount of catalyst was used, the result obtained shows that during the hours the reaction takes place mostly at the *A* part or at the *A* and *B* parts and that the predomination of the reaction at the *C* part takes longer time.

2. The effect of added H_2 or N_2.

The addition of N_2 to NH_3 was found to produce no effect on the decomposition, so far as 10% N_2 in volume was added.

In the case of H_2, 3% H_2 somewhat retards the decomposition velocity, while 10% H_2 produces a remarkable effect. As to the retarding effect of 10% H_2, the ratios of the increases in pressure for 50, 100 and 200 minutes in the decomposition of ammonia were 0.63, 0.67 and 0.70 respectively. The decomposition immediately after the reduction of the catalyst by H_2 also proceeds extremely slowly and is far slower than when retarded by 10% H_2.

3. The effect of added CO.

CO generally acts as a poison. The decomposition curves of the catalyst poisoned with NH_3[5] containing 1% CO (Expt. 6) and that of the catalyst not poisoned (Expt. 2) are compared in Fig. 2. What was once more poisoned

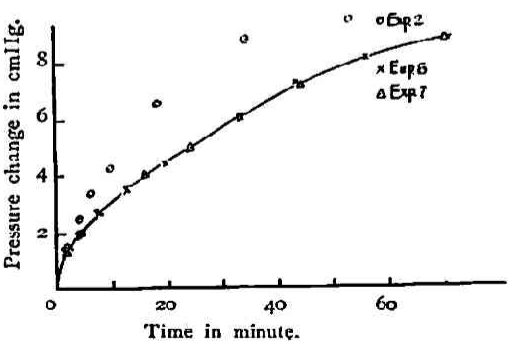

Fig. 2.

5) A gas mixture of CO and NH_3 (the ratio of CO to NH_3, 1%:99%) under 20 cm. Hg was kept in the reaction vessel for 1 day and evacuated and then reduced. After the retardation immediately after the reduction was checked, the decomposition (Expt. 6) was carried out.

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under the same condition (Expt. 7) is as it was, and poisoning does not proceed. This poisoned catalyst was oxidized with the air by introducing the air containing oxygen not so much more excessive than carbon monoxide at the same temperature as in the decomposition and it was then reduced. By the catalyst thus reduced ammonia was decomposed (Expt. 8). The result obtained is shown in Fig. 3 with the $\frac{x}{t}-k_m$ curve in comparison with the former three cases.

Similarly, the experiments after poisoning with 3.5% CO and that after oxidation and reduction (Expt. 10) are shown in Fig. 4. In Expt. 10, being different from Expt. 8, the reaction consists of only two stages.

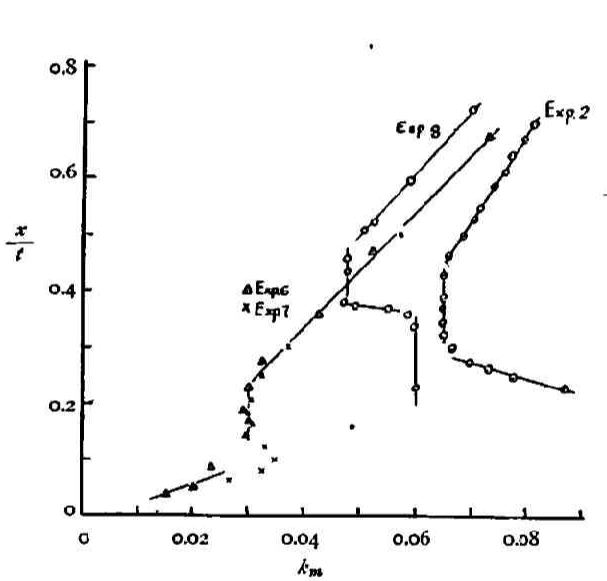

Fig. 3.

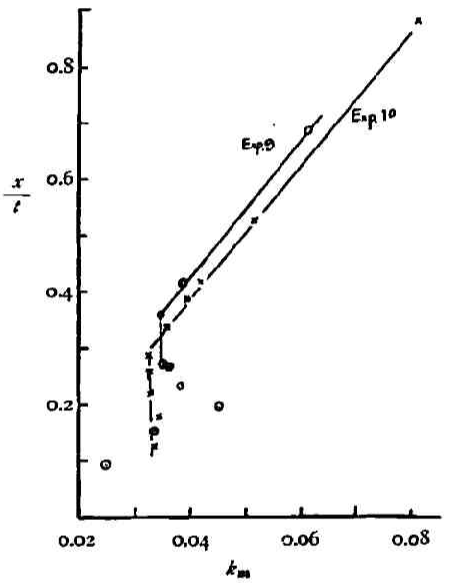

Fig. 4.

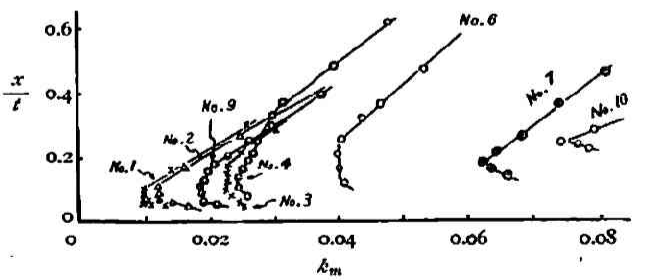

Fig. 5.

The $\frac{x}{t}-k_m$ curve of each catalyst

The $\frac{x}{t}-k_m$ curves of catalyst Nos. 1—10 are shown in Fig. 5, and the points where these curves intersect the $\frac{x}{t}$ and k_m axes shown in Fig. 6.

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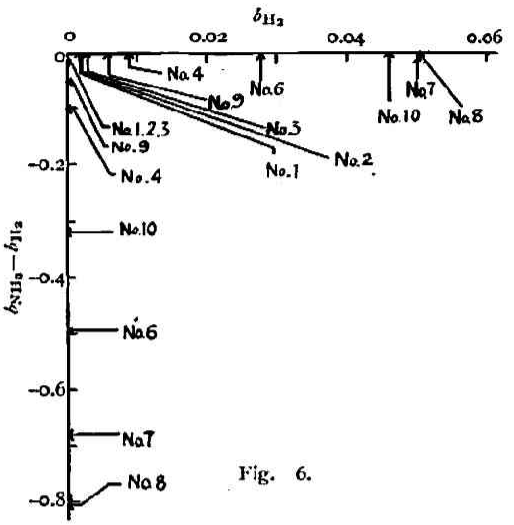

Fig. 6.

Discussion

1. Kobosev,[6] Natanson and other investigators have observed that the reduction of the iron oxide catalyst is retarded in the presence of the promoter Al_2O_3 and elucidated the relation between the retardation of reduction and the promoting action. Namely, it has been pointed out that the stronger the retarding action of reduction is the more active catalyst is obtainable. In the present case, however, Tables I, II, III and V do not indicate the fact that the more intensely the reduction is retarded, the higher the activity is made with increased amount of K_2O or Al_2O_3, that of Al_2O_3 or K_2O being kept constant. It is apparent from this evidence that the relation proposed by them holds good only when one of such substances as Al_2O_3 and BeO which make a solid solution with iron oxide is added. Kobosev has attributed the retardation of the reduction to the accumulation of Al_2O_3 on the surface of the catalyst. It is deduced from the results obtained that K_2O affects the nature of the surface layer of Al_2O_3 and that there exists an optimum concentration of Al_2O_3 or K_2O for the protection of the iron reduced. It is concluded that no simple relation holds between the activity and the retardation of the reduction.

2. When the concentration of K_2O is constant, the increase in the amount of Al_2O_3 leads to the decrease in the adsorbed amount of hydrogen (Table 4). When the concentration of Al_2O_3 is constant, what the increase in the amount of K_2O brings forth is uncertain. Therefore, it seems improbable that the nature of the surface layer of Al_2O_3 is simply related to the adsorption of hydrogen.

3. The value of δ_{H_2} of each catalyst is given by equation (I), and its numerical value is obtained on the abscissa in Fig. 6 from the curve shown in Fig. 5. The enlargement of k_m means the reduction of δ_{H_2}, so that the leaving from the origin shows the reduction of δ_{H_2}, i.e. the decrease in the adsorption of H_2. It is clear from the results obtained that the decomposition of ammonia is

6) Kobosev, *Acta Physicochim. U. R. S. S.*, 4, 829 (1936).

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retarded by H_2. Accordingly, the reduction of b_{H_2} is at least one of the causes to make the activity higher. A comparison between the order of the reduction of b_{H_2} and that of the increase in activity will be drawn as follows:

The order of the reduction of b_{H_2}: (The numbers indicate Catalyst No.)

No. 1→No. 2→No. 3→No. 9→No. 4→No. 6→No. 10→No. 7→No. 8 (i)

The order of the increase in activity:

At $t\left(\frac{1}{4}\right)$,

No. 1→No. 2→No. 3→No. 9→No. 4→Nos. 6, 10 and 7,→No. 8 (ii)

At $t\left(\frac{1}{2}\right)$,

No. 1→No. 2→No. 3→No. 9→No. 4→No. 8→No. 6→No. 10→No. 7 (iii)

At $t\left(\frac{1}{1}\right)$,

No. 2→No. 1→No. 9→Nos. 3 and 4→No. 6→Nos. 10 and 7→No. 8. (iv)

The order of the reduction of $|\, b_{NH_3}-b_{H_2}\,|$:

Nos. 1, 2 and 3→No. 9→No. 4→No. 10→No. 6→No. 7→No. 8. (v)

(i), (ii) and (v).

From (i) and (ii) was obtained the result that the less the adsorbed amount of hydrogen is the more active the catalyst becomes.

It is seen from (ii) and (v) that the order of the approach of the ammonia adsorption to the hydrogen adsorption nearly coincides with the order of the increase in activity. This will be explained below in greater detail.

Let b_{NH_3}, b_{H_2} and the activity $t\left(\frac{1}{4}\right)$ of No. 1, No. 2, No. 3.....be represented by $b^1_{NH_3}$, $b^2_{NH_3}$, $b^3_{NH_3}$,.....; $b^1_{H_2}$, $b^2_{H_2}$, $b^3_{H_2}$,.....; and a^1, a^2, a^3,..... respectively.

As to No. 1, No. 2 and No. 3; we have

$$b^1_{NH_3}-b^1_{H_2}=b^2_{NH_3}-b^2_{H_2}=b^3_{NH_3}-b^3_{H_2}$$

and

$$b^1_{H_2}>b^2_{H_2}>b^3_{H_2};$$

hence,

$$b^1_{NH_3}>b^2_{NH_3}>b^3_{NH_3},$$

where $a^1<a^2<a^3$. These three examples illustrate the case that the activity is low in spite of a large adsorbed amount of ammonia when the adsorbed amount of hydrogen is large.

As to No. 6 and No. 10, we have

$$|\, b^6_{NH_3}-b^6_{H_2}\,| < |\, b^{10}_{NH_3}-b^{10}_{H_2}\,|$$

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and $b^6_{H_2} > b^{10}_{H_2}$;

hence,

$$b^6_{NH_3} > b^{10}_{NH_3},$$

where $a^6 = a^{10}$.

This indicates that though the adsorbed amount of hydrogen is large the activity remains unchanged if the adsorbed amount of ammonia becomes correspondingly large.

As to No. 3, No. 6, No. 7 and No. 8, we have

$$| b^3_{NH_3} - b^3_{H_2} | > | b^6_{NH_3} - b^6_{H_2} | > | b^7_{NH_3} - b^7_{H_2} | > | b^8_{NH_3} - b^8_{H_2} |$$

and $b^3_{H_2} > b^6_{H_2} > b^7_{H_2} > b^8_{H_2}$.

Accordingly, the magnitude of b_{NH_3} can not be decided, but let us consider three cases with respect to No. 3 and No. 6, thus:

$$b^3_{NH_3} < b^6_{NH_3}. \quad \text{(a)}$$

$$b^3_{NH_3} = b^6_{NH_3}. \quad \text{(b)}$$

$$b^3_{NH_3} > b^6_{NH_3}. \quad \text{(c)}$$

where $a^3 < a^6$.

The above relations (a) and (b) tell that the activity is high either when the adsorbed amount of hydrogen is small and that of ammonia is large or when both adsorbed amounts of ammonia and hydrogen are approximate, and yet it is natural to obtain this result at the most highly active part which is subject to the retardation of hydrogen. But we shall choose the 3rd relation in the present case. According to Kagan and Morozov[7], K_2O decreases the heat of adsorption of NH_3 and the activity of adsorption and hinders the condensation of NH_3. Applying this idea to the above-described case where Al_2O_3 is constant and K_2O is increased, we have

$$b^3_{NH_3} > b^6_{NH_3} > b^7_{NH_3} > b^8_{NH_3},$$

where $a^3 < a^6 (= a^7) < a^8$.

Here we come to the same conclusion as drawn for Nos. 1, 2 and 3 or Nos. 6 and 10.

(i), (iii), (v) and (i), (iv) (v).

A comparison between (ii) and (iii) indicates that at the latter half the order of the catalysts differs from each other. As to (iv), the order of each catalyst, as a whole, varies as compared with (ii) and (iii).

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7) Kagan and Morozov, *Acta Physicochim. U. R. S. S.*, **5**, 491 (1936).

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This change of the position depends upon the circumstances that the reaction takes place either at the most highly active part A or even at the less highly active part B or further even at the least active part C. The results obtained showing at which stage of the active parts A, B and C, $t\left(\frac{1}{4}\right)$, $t\left(\frac{1}{2}\right)$, and $t\left(\frac{1}{1}\right)$ of each catalyst lie, are tabulated in Table VI. Judging from Table VI it is no wonder that the relation between b_{H_2} and $b_{NH_3}-b_{H_2}$ shown in Fig. 6, which has been found from the decomposition at the most highly active part A, does not hold good with $t\left(\frac{1}{2}\right)$ and $t\left(\frac{1}{1}\right)$ including the results at the less highly active parts B and C.

Table VI.

Catalyst No.	$\frac{x}{t}\left(\frac{\text{mm.Hg}}{\text{min.}}\right)$					
	$t\left(\frac{1}{4}\right)$	Reactions at active part	$t\left(\frac{1}{2}\right)$	Reactions at active part	$t\left(\frac{1}{1}\right)$	Active part
1	0.09	A (final)	0.08	B	0.03	C
2	0.14	,,	0.10	B	0.03	,,
3	0.18	,,	0.14	B	0.06	,,
4	0.36	,,	0.20	B	0.06	,,
5	—	—	—	—	—	—
6	1.25	A	1.00	A	0.08	,,
7	1.25	A	1.70	A	0.11	,,
8	2.50	A	0.70	A (final)	0.17	,,
9	0.21	A (final)	0.17	B	0.45	,,
10	1.25	A	1.25	A	0.11	,,

4. It is clear that the adsorption of nitrogen took place at 440°C., though its amount was small. Roiter and his coworkers[8] measured the N_2—adsorption of Fe—Mo and Fe—Mo—Al_2O_3 catalysts in the temperature range between −174°C.—450°C. and found that no adsorption occurred at the temperatures in question though only physical adsorption took place at low temperatures. Their question raised as to the formation of nitride (Fe_2N)[9] is not justified merely with their results obtained.

Some of the examples of the adsorption of hydrogen are given in Table IV. The position of the maximum adsorption, the existence of which was found by Roiter and his coworkers, will appear at higher temperatures (above 500°C.). In Table IV a decrease in the adsorbed amount of hydrogen is parallel to the reduction of b_{H_2}, but, there is no exact proportionality between the two in all

8) Roiter, *Acta Physicochim. U. R. S. S.*, 4, 145 (1936).

9) Frankenburger, *Z. Elektrochem.*, 39, 45, 97, 269, 818 (1933).

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the examples. It is not unreasonable that b_{H_2}, being obtained from the reaction velocity at the most highly active part, shows no similarity to the value obtained by the adsorption of hydrogen in equilibrium.

5. Supposing several kinds of the active parts, Langmuir's formula was applied to them, and its applicability was qualitatively justified with respect to each catalyst. As to the most highly active part ($b_{H_2} > b_{NH_3}$), its existence can be ascertained by the experiment carried out by adding 10% H_2 by the retardation immediately after the reduction, or by the fact that each catalyst is retarded at the initial stage of the reaction.

6. The relation between poisoning by CO and the active parts is seen in Fig. 3 and Expts. 6, 7 and 9 in Fig. 4. These figures show that, after the occurrence of the decompositions at the most highly active part and the active part of $b_{H_2}=b_{NH_3}$, the rate of decomposition is increased, i.e. a higher active centre appears. This fact also indicates the removal of poisoning by CO, and it is supposed that hydrogen, the decomposition product, exerts a reactivating action for the poisoned part. Each point at this poisoned part fluctuates, and it may be ascribed to the action of poisoning. The existence of the active part reactivated by air oxidation and hydrogen reduction on this poisoned catalyst is shown by the line perpendicular to the k_m axis in Expt. 8. It is, of course, inactive as compared with the three active parts—A, B and C. Expt. 10 corresponds to Expt. 8 and is the case where the catalyst has been poisoned more severely than in Expts. 6 and 7. This experiment, in which the reaction ends at the active part of the second and the velocity of decomposition falls off markedly, produces a similar result to the case of reaction made in the presence of an extremely small amount of the catalyst.

Summary

1. From the results obtained by applying Langmuir's formula to some supposed kinds of active parts it has been found that the decomposition reaction proceeds in the following order: a reaction of retarded form at first, and of the first order, and then of the zero or the fractional order.

2. As to a catalyst or a group of catalysts having different percentages of the component, the following were measured or examined:

i. the velocity of reduction,

ii. the adsorptions of hydrogen and nitrogen,

iii. the relation between activity and the adsorption coefficients of

hydrogen and ammonia,

iv. the influence of the velocity of decomposition by hydrogen and nitrogen, and

v. poisoning by CO, the removal of the poisoning by oxidation and reduction, and reactivation of the active centres during the reaction.

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